Optical and Tribological Properties of PVD/CVD Diamond-like Carbon Films

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The optical and tribological properties of diamond-like carbon (DLC) films deposited by the combination of magnetron sputtering of graphite and plasmochemical dissociation of methane were studied. It was established that at methane concentration in the gas mixture Ar/CH4 at about 5–10 % the formation of DLC films with refraction index n ≥ 2.0, microhardness larger than 1000 HK and friction coefficient of 0.06–0.08 becomes possible.

Keywords: diamond-like carbon, magnetron sputtering, methane dissociation, refractive index, friction coefficient, microhardness

1 INTRODUCTION

As diamond-like (DLC) films and coatings possess a number of unique properties such as, high microhardness, thermal conductivity, wear resistance, transmittance in the IR range, chemical inertness and biocompatibility, over the past years they have been widely used in optics, opto- and microelectronics, biomedicine, and metal working.

One of the important areas of DLC film application is coating of Ge-based IR optical systems. It was shown that transmission coefficient for germanium lens and windows does not exceed 43 % [1]. Currently applying oxide- and sulfide-based coatings allow for increasing in the transmission coefficient of germanium optics up to 96–98 %. However in some cases the low tribological and mechanical properties of the antireflecting coating are terminated their application. The usage of DLC coatings allows protecting the germanium optics and increasing in its transmission coefficient up to 93–98 % as well. At the same time at 90 % level the width of transmission range can reach up to 2.5 μm.

At present time the DLC films and coatings are obtained by chemical vapor deposition (CVD) of hydrocarbons and physical vapor deposition (PVD) by graphite sputtering. For CVD methods the number of substrates is terminated as optimal temperature of substrate for DLC crystallization is about 900 ºC. Unlike CVD in PVD methods the films are deposited at low temperatures this allows for using the plates of any type, *e.g.*, plastics, glasses [3–6]. Among PVD methods the unbalanced magnetron (UMB) sputtering should be marked as this method can provide low energy ion bombardment of growing film alongside with high rates of deposition. Ion bombardment allows for controlling the properties of the coatings obtained and plays an important role in processes of formation of carbon atoms in sp^3-hybridization [7]. Besides, in case of UBM sputtering unbalanced magnetic field generates in the space of target–substrate semi-self-maintained discharge that can be used in CVD for DLC films deposition.

So we aimed to study optical and tribological characteristics of DLC films on Si and glass substrates obtained by the combination of PVD and CVD when as carbon source methane and graphite were used for films' prospective application as antireflecting and protective coatings for germanium IR optics.

2 EXPERIMENTAL

The schematic diagram of experimental setup for deposition of DLC films by combination of PVD/CVD is shown in Fig. 1. The chamber of vacuum setup was equipped by UBM where the change in configuration and intensity of magnetic field in the area target–substrate was achieved by magnetic field of the additional solenoid that allows for changing in the level of magnetron unbalance in wide range [8, 9].

Si (100) and optical glass BK7 were used as substrates that were placed at a distance of 8.5 cm from the UBM target surface. The chamber of vacuum setup was pumped out up to the residual pressure of 10^{-3} Pa. Before the deposition the substrates were cleaned by ion beam generated by Hall current ion source. The source was supplied by Ar up to the working pressure 2.0×10^{-2} Pa. During all experiments the clearing time, ion energy and discharge current were of 3 min, 700 eV, 40 mA, respectively.

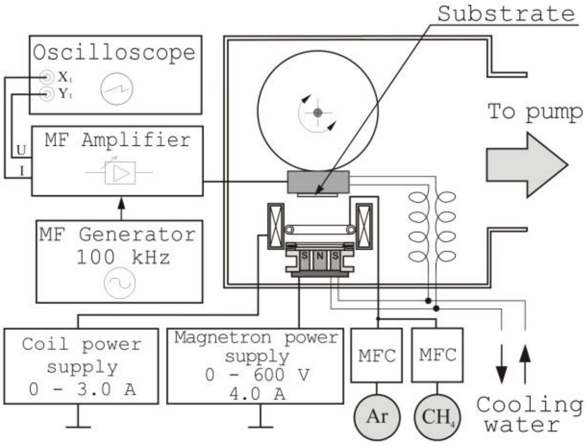

Fig. 1: The schematic diagram of experimental setup for deposition of DLC films by combination of PVD/CVD

The sputtering of graphite target (99.95 %), ∅ 80 mm was carried out by magnetron sputtering Ar/CH_4 mixture was used as working gas. For additional methane destruction and control of energy of ion bombardment of film the middle frequency (MF) bias (alternating current 100 kHz at amplitude of 800 V) of the substrate was used. At the same time the UBM discharge generated the ions sputtered the material of the target and activated the dissociation of methane as well. The methane concentration in Ar/CH_4 mixture was changed in the range of 0–20 % with total flow rate 70 sccm; in the chamber the pressure was 0.1 Pa. The mass flow control RRG-1 was used to control the flow rate of the gases. The power supply of 1.5 kW with the possibility of stabilization of current and power was used. The UBM current discharge was 0.25 A. The films were deposited up to the thickness of 0.8–1.6 μm. The thickness of the layers was determined by the optical interferometric profilometer POI–08. Optical characteristics of the deposited films were measured by ellipsometer LEF-3M-1 at wavelength of 0.63 μm and angle beam of 65º to the normal. The values of microhardness of DLC films were taken by Leika VMHT Mot by Knoop hardness test at indenter load of 5 g and time of load retaining of 20 s. The coefficient of friction was measured by tribometer RPT-02 by the wearing of film with indenter (steel sphere with the diameter of 5.0 mm) under the conditions of dry friction. The indenter load was 0.58 N.

3 RESULTS AND DISCUSSION

The dependences of deposition rate, discharge voltage on methane concentration in gas mixture Ar/CH_4 and amplitude of MF substrate bias were determined. While methane concentration was increased the discharge voltage was decreased from 640 to 570 V. The deposition rate was almost independent on methane concentration in the gas mixture Ar/CH_4 and amplitude of substrate bias.

During graphite sputtering in Ar atmosphere the deposited films have high internal stress and when the film thickness reaches 200 nm the films are exfoliated. When the CH_4 was added the critical thickness of DLC coating was increased at least up to the value of 1.6 μm.

When in the mixture of working gases the methane concentration was increased from 3.5 to 18 % the refraction index of DLC coatings was steady decreased from 2.28 to 1.94 (Fig. 2). Absorption coefficient was at about 0.10–0.18 and was independent on the concentration of methane. It should be noted that the described results were obtained at impulse substrate bias with amplitude of 600 V and discharge magnetron current of 0.25 A. The refraction coefficient of the films formed at higher discharge current and U_S was not larger than 1.84.

The values of microhardness of DLC films on Si substrate were 800–1100 HK (Fig. 3). The microhardness of the films was increased when the concentration of the methane was decreased. The dependences of friction coefficient μ on the number of reciprocations are shown in Fig. 4. As can be seen from Fig. 4, slip distance can be divided into three regions. The first one indicates the wear-in stage. At this stage the friction coefficient is abruptly increased up to the value of 0.15–0.2 and then after 100–150 reciprocations is decreased up to the constant value. In the second region the stage of steady-state wear was observed and the friction coefficient was at about 0.06–0.085 and was slightly changed in the case of the DLC films formed at different methane concentration. In the third region is characteristic for samples obtained at low methane concentration (less than 5 %) (see Fig. 4 *a*). For these samples after 700–1200 reciprocations friction coefficient was abruptly increased and reached the value of the initial plate that indicates the relatively low tribological properties of these films. DLC films deposited at high methane concentration passed all test cycles (5000 reciprocations) without change in friction coefficient (see Fig. 4 *b*).

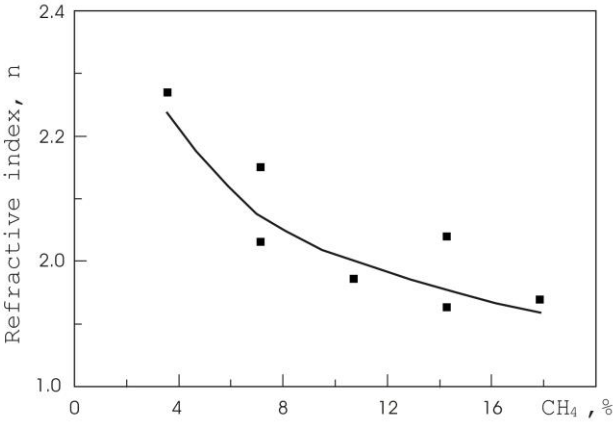

Fig. 2: The dependance of refraction index of the DLC films on the concentration of methane in the gas mixture Ar/CH_4

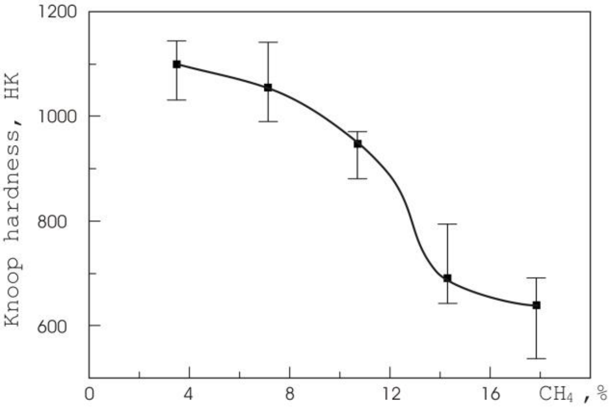

Fig. 3: The dependence of microhardness of DLC films on the concentration of methane in the gas mixture Ar/CH_4

Apparently the increase in methane concentration in gas mixture results in the increase in hydrogen concentration in the deposited films due to partial dissociation of CH_4 in the UBM discharge. The increase in hydrogen content leads to the increase in the possibility of carbon polymer chains formation with $n \leq 1.6$ [9] and consequently to the decrease in refraction index and microhardness of the films. However the growth of hydrogen content results in the increase in the wear resistance of DLC films.

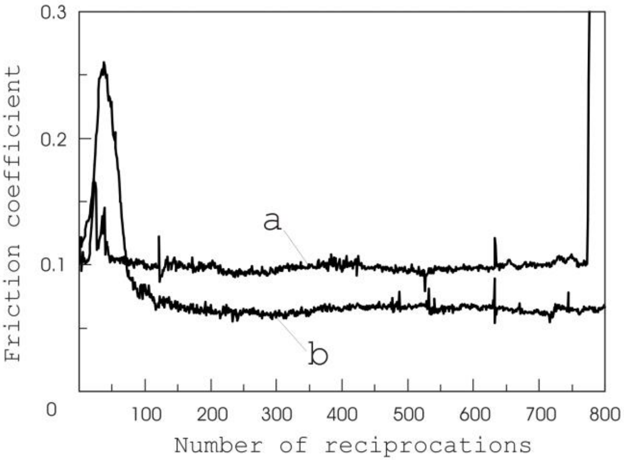

Fig. 4: The dependences of the friction coefficient of DLC films on the number of reciprocations at a different methane concentration in Ar/CH_4 gas mixture: a – 3.5 % b – 7.0 %

4 CONCLUSIONS

DLC films were obtained by the combination of PVD and CVD methods. Hydrocarbons dissociated in UBM glow-discharge plasma and sputtered graphite target were used as carbon sources. It was established that at methane concentration in the gas mixture Ar/CH_4 at about 5–10 % the formation of DLC films with refraction coefficient $n \geq 2.0$, microhardness larger than 1000 HK and friction coefficient of 0.06–0.08 becomes possible. At the same time the film thickness can exceed 1.0 μm that allows for using these films as protective and antireflective coatings for germanium based IR optics.

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